MS19-P18 A new high flux neutron backscattering spectrometer for research into the ns-dynamics of battery, fuel-cell and hydrogen storage materials.

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The new neutron backscattering spectrometer IN16B at the Institut Laue-Langevin, Grenoble, with highest flux and signal-to-noise ratio for a high energy resolution spectrometer of its kind, is perfectly suited for studying diffusion and relaxation processes on the nanosecond time scale. In this poster we also present some instrumental aspects, but will mainly give examples to illustrate the possibilities for spectroscopy on materials which are of interest for fuel cells, battery materials or hydrogen storage.

IN16B has a standard energy resolution with Si111 analysers in backscattering of FWHM ~ 0.75 μeV in an energy transfer range of ± 30 μeV, thus exploring simultaneously a momentum transfer (Q) range between 0.2 and 1.8 $Å^{-1}$. The Q-range can be doubled by using Si311 analysers and the resolution can be halved by using unstrained small crystals on the analyser sphere. Ongoing projects aim for an energy transfer range extension by a factor of 10 with BATS, BAckscattering and Time-of-flight Spectrometer and a decade improvement of the energy resolution.

Keywords: neutron spectroscopy, energy related materials, dynamics, relaxation

MS20 Materials for energy conversion and harvesting

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MS20-P1 Organic-inorganic hybrid perovskite $CH_3NH_3PbI_3$: structural consequences of water absorption

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The organic-inorganic hybrid perovskite-like $CH_3NH_3PbI_3$ ($MAPbI_3$) is intensively studied owing to its role in energy conversion. In this compound, the linear methyl ammonium (MA^+) cation is located in the centre of the cuboctahedra formed by I-atoms. Hence, statistical disorder over its different orientations can be expected. This allows a high flexibility of the structure symmetry with pressure, temperature and other conditions affecting the weak N-H...I hydrogen bonds, which maintain this cation inside the cuboctahedron. Indeed, the different tetragonal space groups, such as *I*4/*mcm* [1-4], *I*4*cm* [5,6] and *I*4/*m* [7], were reported previously even in the room temperature phase. $MAPbI_3$ is structurally unstable at ambient conditions. Air humidity provokes its gradual decomposition. We have studied the mechanism for the decomposition. Crystal structure of the pristine (**I**) and in wet air aged (**II**) samples has been investigated at 293 K with high precision single crystal XRD experiments using synchrotron radiation. We show [8] that different space groups, *I*422 and $P4_32_12$, characterize **I** and **II** , respectively. Both of them are subgroups of *I*4/*mcm*, which is commonly adopted for $MAPbI_3$. The difference appears due to the changes in H-bonds induced by the H_2O inclusion in the structure of the aged crystal **II**. This inclusion initiates the crystal decomposition, which can be described by the chemical reaction: $CH_3NH_3PbI_3$ + (H_2O) = CH_3NH_2+ PbI_2 + (H^+ + I^- + H_2O). The dashed contour in the figure 1 indicates the atomic part, which most probably leaves the structure leading to the decomposition.

[1] Y. Kawamura *et al*., Journal of the Physical Society of Japan, **71**(7), 1694 (2002).

[2] Y. Yamada *et al*., Journal of the American Chemical Society, **137**, 10456 (2015).

[3] Y. Dang *et al*., CrystEngComm, **17**, 665 (2015).

[4] M.T. Weller *et al*., Chem. Commun. **51**, 4180 (2015).

[5] C.C. Stoumpos *et al*., Inorg. Chem. **52**, 9019 (2013).

[6] J. Xie *et al*., Journal of Power Sources, **285**, 349 (2015).

[7] T. Baikie *et al*., J. Mater. Chem. A**1**, 5628 (2013).

[8] A. Arakcheeva, D. Chernyshov, M. Spina, L. Forro, E. Horvath. *$CH_3NH_3PbI_3$: precise structural consequences of water absorption at ambient conditions* Acta Cryst. B. (Submitted in April, 2016).

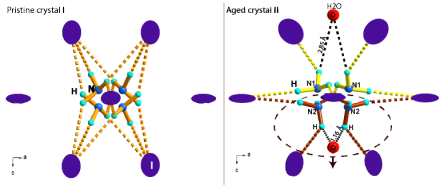

Figure 1. The N-H…I H-bonds in the pristine and the aged crystals. Four shown NH_3 groups conform to four orientations of MA^+. In I, all NH_3 groups are statistically present with probability of 25% for each one. In II, $N2H_3$ and $N1H_3$ are present with probability of 29.5% and 16.5%, respectively.

Keywords: crystal structure, hybrid organic-inorganic lead iodide, aged MAPbI3

MS20-P2 Thermoelectric transport properties in magnetically ordered crystals

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Thermoelectric transport properties of magnetically ordered crystals in an external magnetic field **H** were investigated in [1, 2] from a space-time symmetry point of view. Crystals belonging to any of the 122 point groups may show electric resistivity, thermal conductivity, Seebeck and Peltier effect for **H**=0, as well as the following effects linear in **H**: Hall, Righi-Leduc, Nernst and Ettingshausen. The tensors describing these effects are invariant under space inversion $\underline{1}$ and time inversion 1'; their form can be found using Neumann's principle and the Onsager relations $\Gamma_{\mu\nu}(\mathbf{H}) = \Gamma_{\nu\mu}(-\mathbf{H})$, where Γ is a 6×6 matrix giving the gradient of the electrochemical potential and the heat current as functions of the electric current and the temperature gradient in the crystal.

Magnetically ordered crystals belong to one of the 90 magnetic point groups (MPGs) that do not contain time inversion 1' as a separate element. For **H**=0, spontaneous Hall and Righi-Leduc effects appear for the 31 MPGs allowing ferromagnetism; spontaneous Nernst and Ettingshausen effects appear for 58 MPGs. Whereas magnetoresistance, magneto-heat-conductivity, magneto-Seebeck and magneto-Peltier effect are of even order in **H** in magnetically unordered crystals, such effects linear in **H** appear in case of magnetoresistance and magneto-heat-conductivity for the 66 MPGs allowing piezomagnetism, and in case of magneto-Seebeck and magneto-Peltier effect for all 69 MPGs that do not contain space-time inversion 1' as a separate element.

To find the forms of the tensors describing the effects in magnetically ordered crystals, Onsager relations were used in [1] as formulated in [3]: $\Gamma_{\mu\nu}(\mathbf{H}, \mathbf{M}) = \Gamma_{\nu\mu}(-\mathbf{H}, -\mathbf{M})$, where **M** denotes the time averaged magnetization field describing the magnetic configuration.

Whereas the results of [1] and [2] agree for **H**=0, some of the results obtained in [2] for the effects linear in **H** are at odds with generally accepted results. The procedure used in [1] makes it easy to separate tensors into two parts being invariant and changing sign under 1', respectively. Whereas [2] considers both parts as forming a single tensor, it will be shown that considering the two parts (which can be measured separately) as independent tensors leads to simpler and stronger results.

References:

[1] H. Grimmer (1993). *Acta Cryst*. A**49**, 763-771.

[2] M. Seemann, D. Ködderitzsch, S. Wimmer & H. Ebert (2015). *Phys. Rev. B*, **92**, 155138.

[3] S. Shtrikman & H. Thomas (1965). *Solid State Commun*. **3**, 147-150.

Keywords: Thermoelectrics, Transport properties, Onsager relations, Magnetic order